A combined reaction class approach with integrated molecular orbital+molecular orbital (IMOMO) methodology: A practical tool for kinetic modeling

Thanh N. Truong,[a] Dilip K. Maity, and Thanh-Thai T. Truong
Henry Eyring Center for Theoretical Chemistry, Department of Chemistry, University of Utah, 315 S 1400 E, Room Dock, Salt Lake City, Utah 84112

(Received 16 August 1999; accepted 5 October 1999)

We present a new practical computational methodology for predicting thermal rate constants of reactions involving large molecules or a large number of elementary reactions in the same class. This methodology combines the integrated molecular orbital+molecular orbital (IMOMO) approach with our recently proposed reaction class models for tunneling. With the new methodology, we show that it is possible to significantly reduce the computational cost by several orders of magnitude while compromising the accuracy in the predicted rate constants by less than 40% over a wide range of temperatures. Another important result is that the computational cost increases only slightly as the system size increases. © *2000 American Institute of Physics.* [S0021-9606(00)00201-4]

I. INTRODUCTION

One of the great challenges in computational science in the new millennium is bridging the gap in time scale from femtoseconds to minutes or hours and in spatial scale from angstroms to meters. An example of such a challenging problem is the simulation of fire from a pool of hydrocarbon fuel with a diameter on the order of meters and monitoring all important chemical species from the combustion process including soot formation and heat transfer processes. This presents numerous challenges both in computational engineering and in fundamental chemistry. From the fundamental chemistry perspective, to satisfy the requirement of a rather detailed kinetic model for the combustion of hydrocarbon fuel as well as soot formation is a difficult task since these kinetic models consist of the order of thousands of elementary reactions, many of whose kinetic parameters are not known for certain. From an environmental point of view, as the quest for cleaner industrial processes continues, the demand for more complete kinetic models increases since the minor products (contaminants or toxic wastes) become a more important issue rather than the major products. To improve the completeness and accuracy of a kinetic model of any combustion process is a scientific challenge. It is apparent that computational chemistry can play a significant role here.

Progress in computational chemistry, particularly development of *ab initio* direct dynamics methods,[1–20] shows promise for predicting accurate thermal rate constants of polyatomic gas-phase reactions. It is now possible to predict quantitatively rate constants for reactions of moderate size of less than six heavy atoms. The demand for reasonable kinetic parameters for a large number of elementary reactions in a reasonable time frame puts a restriction on the level of theory that can be employed. In practice, the main source for getting these rate constants theoretically is from the framework of the simple conventional transition state theory (TST). The TST methodology has known deficiencies. In particular, it does not include the recrossing effects that are important in the high-temperature region for reactions with low barriers and cannot adequately model the quantum mechanical tunneling effects that have significant contributions in the low-temperature region in many combustion reactions. Unfortunately, to obtain more accurate rate constants, much more potential energy information is required than what is normally needed for TST calculations. A better theoretical approach is the variational transition state theory (VTST)[21–27] augmented by multidimensional semiclassical small-curvature tunneling corrections.[25,28] This method requires energy, gradient, and Hessian information along the reaction path. This information can be costly, particularly for large systems if such potential energy information is to be calculated directly at a sufficiently high level of theory in the direct *ab initio* dynamics methodology. There have been several procedures developed recently attempting to reduce such cost. One is to use a semiempirical Hamiltonian as an analytical potential energy function with specific parameters fitted to accurate single-point energy calculations at selected points along the minimum energy path (MEP).[17,18,29] With this potential energy function, one can perform full canonical variational TST (CVT) calculations with accurate tunneling models. Another is based on the fact that energy converges more slowly with respect to the level of theory than geometry and frequency. Thus, one can calculate geometries, gradients, and Hessians at a low level of theory while the energy along the MEP can be corrected by a series of single-point calculations at a high level of theory.[19,30,31] Even then, 10 to 20 single-point energy calculations at a sufficiently accurate level, which is often at the level of MP4 or better, are still

[a]Electronic mail: truong@chemistry.chem.utah.edu

computationally demanding, particularly for moderately large systems with more than four heavy atoms.

To circumvent this problem, particularly for large systems, one can employ the ONIOM approach proposed by Morokuma and co-workers.[32–36] This approach, encompassing both the IMOMO and IMOMM models, combines layers of different levels of MO theory and molecular mechanics force fields to achieve an optimal cost/performance strategy in obtaining structural and energetic information. In this approach, a small subregion of the whole system that is most critical to the particular chemical properties of interest is treated at an accurate level of theory; the remaining spectator region can be treated at a lower level in order to achieve computational efficiency. This approach has shown considerable promise so far.[32–37] An important note is that in the ONIOM approach, the division of the whole system into subsystems is left entirely to the chemical intuition of the user. In our recent study,[38] we found that use of the ONIOM methodology can provide a cost-effective way to improve energetic information along the MEP, particularly in the transition state region.

Similar to the ONIOM method in aims is the reaction class approach[39] that we recently proposed for predicting thermal rate constants of chemical reactions involving large molecules or a large number of similar elementary reactions with a high level of efficiency. The central idea comes from recognizing that reactions that have the same reactive moiety have similar features on their potential energy surfaces along that particular reaction path direction. Thus, we can transfer certain potential energy information from the principal reaction (the smallest reaction in the class) to larger reactions in the same class without having to calculate it explicitly. Consequently, we can save an enormous amount of time and computational cost.

Our main interest in this study is in kinetics. The main focus is to illustrate how the IMOMO method can be combined with the reaction class approach in canonical variational transition state theory (CVT)[24,25] rate calculations of different reactions in the same class. We will examine accuracy and efficiency of different schemes that allow one to improve the TST rate constant when it is necessary but with minimal additional cost.

II. METHODOLOGY

The reaction class approach is a general concept which can be used to estimate both the recrossing and tunneling effects. However, we will concentrate in this study on its use in tunneling contribution for the following reasons. First, tunneling often can enhance the rate by several orders of magnitude in the low-temperature range while the recrossing effect lowers the rate typically by a factor of 2 or 3 at most at high temperatures. Thus, the impact of tunneling on the overall rate of the reaction is more significant. Second, tunneling requires potential energy information in a broader range of the reaction coordinate than the recrossing effect, since the latter depends on the location of the variational transition state which varies in a smaller range of the reaction coordinate depending on the temperature. Consequently, the tunneling effect would provide a much more severe test of the reaction class approach.

Within the framework of TST and VTST, motion along the reaction coordinate is treated classically while vibrational motions perpendicular to this degree of freedom are treated quantum mechanically. Quantum mechanical effects in the reaction coordinate motion are represented by the temperature-dependent transmission coefficient $\kappa(T)$. Within the TST formalism, the tunneling effect can be estimated either from the Wigner correction or Eckart model. The Wigner model depends only on the imaginary frequency of the transition state and is known to often grossly underestimate the tunneling effect since it only accounts for contributions near the top of the barrier. The Eckart model, described in more detail elsewhere,[40] gives more accurate tunneling contribution. However, its accuracy is sometimes questionable due to cancellation of errors as discussed in our recent study[39] and also in a later section of this paper. More accurate treatments of tunneling effects require potential energy information along the tunneling path. Within the centrifugal-dominant small-curvature semiclassical adiabatic ground-state tunneling approximation (SCT),[23,28] the effective potential for tunneling can be approximated by the vibrationally adiabatic ground-state potential given by

$$V_a^G(s) = V_{\mathrm{MEP}}(s) + V_{\mathrm{int}}(s), \tag{1}$$

where $V_{\mathrm{MEP}}(s)$ is the potential energy along the minimum energy path (MEP); $V_{\mathrm{int}}(s)$ denotes the total zero-point energy at s,

$$V_{\mathrm{int}}(s) = \sum_{i=1}^{3N-7} \frac{1}{2}\hbar\omega_i(s), \tag{2}$$

with ω_i denoting the frequency of mode i and the summation is over $3N-7$ vibrational modes orthogonal to the reaction coordinate at s where N is the number of atoms. Here, the reaction coordinate s is defined as the distance along the MEP with the origin located at the transition state and the positive direction toward the product. From the SCT method the transmission coefficient is approximated as the ratio of the thermally averaged multidimensional semiclassical transmission probability $P(E)$ to the thermally averaged classical transmission probability for scattering by the effective potential $V_a^G(s)$, and is given by

$$\kappa(T) = \frac{\int_0^\infty P(E) e^{\{-E/k_bT\}} dE}{\int_{E^*(T)}^\infty e^{\{-E/k_bT\}} dE}, \tag{3}$$

where k_b is the Boltzmann constant, and $E^*(T)$ denotes the value of V_a^G at the bottleneck. The transmission probability $P(E)$ is expressed as

$$P(E) = \frac{1}{(1+e^{2\theta(E)})}, \tag{4}$$

where $\theta(E)$ is the imaginary action integral evaluated along the tunneling path and is expressed as

$$\theta(E) = \frac{2\pi}{h}\int_{s_1}^{s_r} \sqrt{2\mu_{\mathrm{eff}}(s)|E - V_a^G(s)|}\, ds, \tag{5}$$

where s_1 and s_r are the reactive classical turning points and $\mu_{\text{eff}}(s)$ is the effective reduced mass that includes the reaction path curvature, i.e., corner cutting effects. The explicit expression for it is not critical for this discussion and can be found elsewhere.[28] In order to calculate the transmission coefficient, one needs to determine the $V_a^G(s)$ and $\mu_{\text{eff}}(s)$. These two terms require energy, gradient, and Hessian information along the reaction coordinate. Calculating this information is computationally quite demanding. Below, we describe several reaction class models for approximating the $V_a^G(s)$ and $\mu_{\text{eff}}(s)$ terms. Thus, these reaction class models are approximations to the SCT method.

A. Reaction class models

The reaction class approach is based on one fundamental postulate: all reactions in the same class share certain similarities on their potential surfaces along their reaction coordinates. The models given below not only describe a hierarchy of approximations but are also designed to test the above postulate. These models assume that $V_a^G(s)$ and $\mu_{\text{eff}}(s)$ functions for the principal reaction, the smallest reaction in the class, are available. Due to the size of the principal reaction, these functions can be easily obtained. In all reaction class models for tunneling given below, we assume that $\mu_{\text{eff}}(s)$ is the same for all reactions in the class, i.e., the reaction path curvature is the same. Since the reaction path curvature components are largest for the reactive modes which result mainly from motions of atoms in the reactive moiety, this approximation is quite reasonable.

1. Model RC-μV

This model is based on two fundamental approximations: (1) $\mu_{\text{eff}}(s)$ is the same for all reactions in the class, and (2) $V_a^G(s)$ has a similar shape for all reactions in the class. Thus, $V_a^G(s)$ for a specific reaction can be determined by scaling the $V_a^G(s)$ of the principal reaction to obtain the correct barrier. This approximation includes the electronic effects of substituents explicitly on the barrier height but only effectively on the barrier width.

This model requires only energy and frequency information for the reactant(s), transition state, and product(s) for the specific reaction. Thus, beside the information of the principal reaction, for a specific reaction no additional information beyond that needed for calculations of TST rate constants is required.

2. Model RC-μi

From detailed analysis we found that the transmission coefficient is much more sensitive to the $V_a^G(s)$ potential than the effective reduced mass $\mu_{\text{eff}}(s)$. Thus, to improve the accuracy of the RC-μV model, we need to pay more attention to $V_a^G(s)$ rather than to $\mu_{\text{eff}}(s)$. Thus, this model makes the same approximation for $\mu_{\text{eff}}(s)$ as in the RC-μV model. However, for the $V_a^G(s)$, it assumes that reactions in the same class have similar width in the directions perpendicular to the reaction coordinate. To be more precise, this approximation assumes that the inactive generalized vibrational modes do not change as functions of the reaction coordinate; only the active modes do and the changes are similar for all reactions in the class. Since inactive modes often do not couple to the reaction coordinate, this approximation is reasonable. In this case, $V_{\text{int}}(s)$ for a specific reaction can be obtained from scaling that of the principal reaction to go through the value at the transition state. Consequently, $V_a^G(s)$ is determined from the explicitly calculated V_{MEP} and the scaled $V_{\text{int}}(s)$.

This model requires not only energy and frequency information at the reactant(s), transition state, and product(s) but also the potential energy V_{MEP} along the minimum energy path.

B. IMOMO model within the reaction class framework

Within the reaction class framework, the IMOMO model system consists of only atoms in the reactive moiety, namely atoms whose nature of chemical bonding changes during the course of the reaction, and capped hydrogen atoms required for saturating the valency. This is the smallest model of the real system that one can partition for a high level of theory treatment. The remaining atoms in the system are treated at the low level in a two-layer IMOMO model.[34]

In our common practice of calculating rate constants, the low level of theory is used to provide geometry, gradient, and Hessian information along the MEP. This requires the low level to be sufficiently accurate so that a single-point energy correction does not noticeably shift the location of the transition state and thus make the improved potential energy along the MEP out of synch with the generalized frequencies calculated at the low level. Such a shift in the location of the transition state may be noticeable in the IRCMAX (intrinsic reaction coordinate for the maximum of energy) methodology.[41]

C. Test cases

We have selected three hydrogen abstraction reactions to test our methodology, namely

$$\mathbf{H}+\mathbf{H}-\mathbf{C}H_2F \rightarrow H_2+CH_2F, \tag{R1}$$

$$\mathbf{H}+\mathbf{H}-\mathbf{C}HF_2 \rightarrow H_2+CHF_2, \tag{R2}$$

$$\mathbf{H}+\mathbf{H}-\mathbf{C}F_3 \rightarrow H_2+CF_3. \tag{R3}$$

The bold atoms in the reactants designate the reactive moiety. These reactions belong to the same class and have classical barrier heights that vary by 3 kcal/mol and reaction energies that differ by more than 5 kcal/mol due to a different number of fluorine atom substituents. They are known to have significant tunneling contributions and thus will provide rather stringent tests on the approach proposed here. Furthermore, accurate rate constants were recently reported[42] and can be used for comparisons.

All three reactions R1–R3 have the same model for high-level calculations, namely the $H+HCH_3$ reaction which is the principal reaction of this class.

D. Computational details

Geometries, gradients, and Hessians of reactants, products, transition states, and along the MEP were determined using the hybrid nonlocal Becke's half-and-half exchange[43]

TABLE I. PMP4/cc-pVTZ and IMOMO(PMP4/cc-pVTZ:BH&HLYP/cc-pVDZ) reaction energies, ΔE, and classical barrier heights, $\Delta V^{\neq}$, and errors $\Delta\Delta E_r$[a] in kcal/mol.

	ΔE			$\Delta V^{\neq}$		
Reactions	PMP4	IMOMO	$\Delta\Delta E_r$	PMP4	IMOMO	$\Delta\Delta E_r$
$H+HCH_2F$	−0.87	−1.29	0.42	12.61	12.45	0.16
$H+HCHF_2$	−0.48	−1.04	0.56	12.58	12.43	0.15
$H+HCF_3$	4.61	4.38	0.23	15.49	15.63	−0.14

[a]Error$=\Delta\Delta E_r=\Delta E$(PMP4)$-\Delta E$(IMOMO) or $\Delta V^{\neq}$(PMP4) $-\Delta V^{\neq}$(IMOMO).

(as implemented in the G98 program[44]) and Lee–Yang–Parr correlation[45] functionals denoted as BH&HLYP with the cc-pvdz[46] basis set. Spin-projected fourth-order Møller–Plesset perturbation theory (PMP4) with the cc-pvtz[46] basis set is used as the high level. Thus, the IMOMO energy is given by

$$\begin{aligned} E(\text{IMOMO}) &= \text{IMOMO(PMP4/cc-pvtz:BH\&HLYP/cc-pvdz)} \\ &= E(\text{PMP4/cc-pvtz;model}) \\ &\quad + \{E(\text{BH\&HLYP/cc-pvdz;real}) \\ &\quad - E(\text{BH\&HLYP/cc-pvdz;model})\}. \end{aligned} \tag{6}$$

For the RC-μi model, MEP calculations are done in the mass-weighted Cartesian coordinate with the sufficiently small step size of 0.01 $\text{amu}^{1/2}$ bohr for a total of 200 steps using the Gonzalez–Schlegel method.[47] This step size is found to be sufficient for the convergence of the variational rate constant as mentioned in our previous study.[31] To improve the energetic information along MEP IMOMO(PMP4/cc-pvtz:BH&HLYP/cc-pvdz) calculations at six different selected points along MEP excluding the transition state were performed. These points were generated by an automated method as implemented in the THERATE program.[31] Note that seven refined energy points along the MEP including the transition state are often the minimum requirement. Thus, it will give a lower bound on the efficiency factor for the new approach as discussed below. All electronic structure calculations were done using the G98 program.[44] Rate calculations were done using the THERATE program.[31]

III. RESULTS AND DISCUSSION

First, it is important to point out that the focus of this study is on the accuracy of the IMOMO model and its combination with the reaction class approach, and not on the accuracy of the calculated thermal rate constants in comparison with available experimental data. The latter was discussed in detail in our previous study[42] where thermal rate constants for R1–R3 reactions were predicted from full CVT/SCT calculations with potential energy obtained from the PMP4/cc-pvtz//BH&HLYP/cc-pvdz level. In fact, we use these calculated rate constants denoted as (full) as a reference point for the comparisons on the accuracy of different approximate models presented here.

The calculated reaction energies and classical barrier heights are listed in Table I. V_{MEP} potential energy curves for all three R1–R3 reactions plotted versus the reaction coordinates are shown in Figs. 1(a)–(c). An important conclusion from these results is that the IMOMO method is able to reproduce the reaction energies, barrier heights, and potential curves from accurate full high-level calculations with less than 1 kcal/mol error. With the enormous saving in the computational cost, the performance of the IMOMO method is in fact excellent.

We now turn our attention to the performance of the reaction class models for tunneling. Figures 2(a)–(c) show log plots of the transmission coefficients calculated from different models versus the temperature for R1–R3 reactions, respectively. We use our previous full SCT results as a reference point where $\mu_{\text{eff}}(s)$ was calculated from BH&HLYP/cc-pvdz Hessian and gradient information; $V_a^G(s)$ was calculated from PMP4/cc-pvtz//BH&HLYP/cc-pvdz potential energies and BH&HLYP/cc-pvdz frequencies. It is perhaps more informative to discuss the performance of each ap-

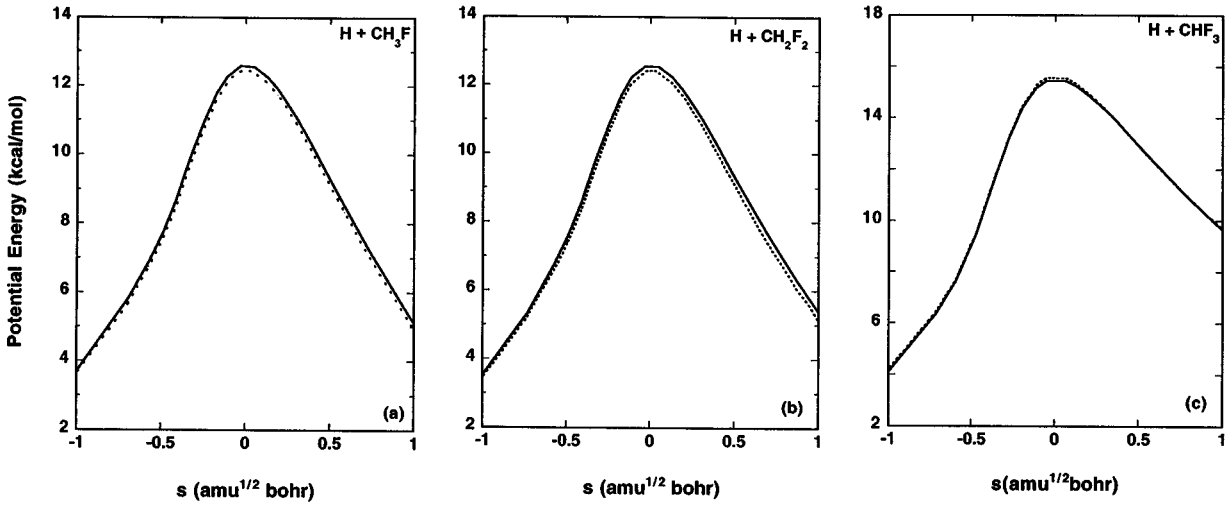

FIG. 1. Potential energy curves plotted versus the reaction coordinate. Solid lines are from the PMP4/cc-pvtz//BH&HLYP/cc-pvdz calculations. Dotted lines are from IMOMO(PMP4/cc-pctz:BH&HLYP/cc-pvdz) single-point calculations at the BH&HLYP/cc-pvdz geometries along the MEP. (a) for the $H+CH_3F$ reaction; (b) for the $H+CH_2F_2$ reaction; (c) for the $H+CHF_3$ reaction.

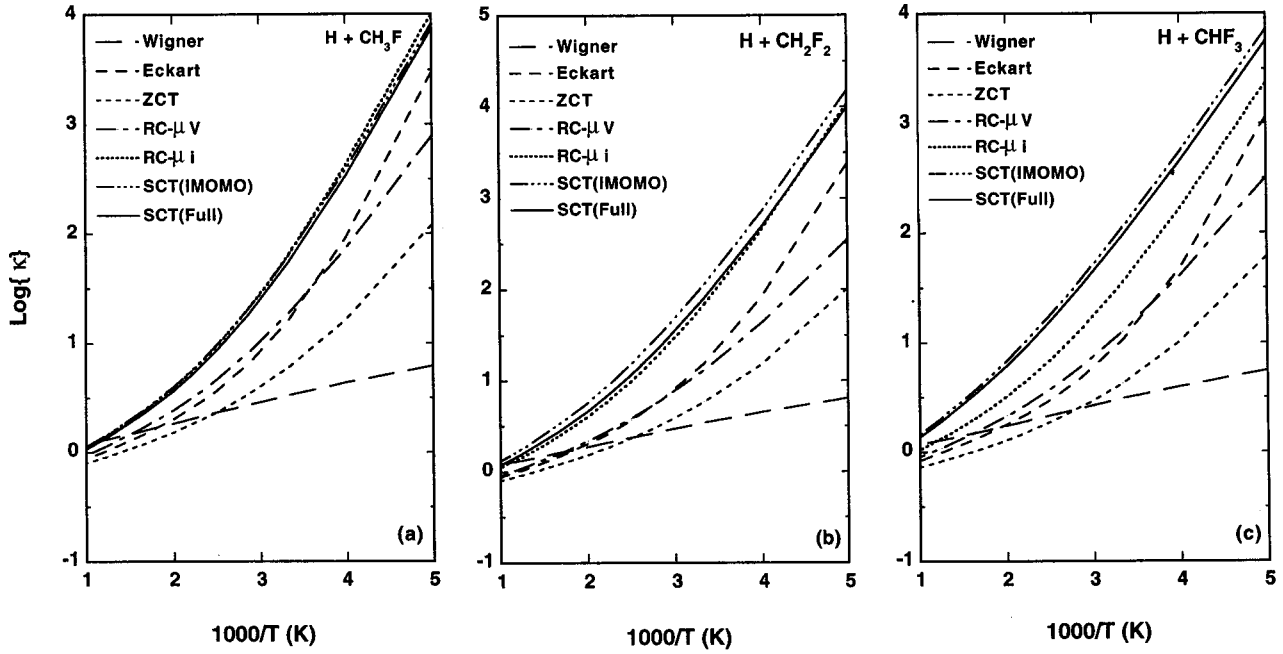

FIG. 2. Plots of $\log_{10}$ of the transmission coefficients κ calculated from different methods versus $1000/T(\mathrm{K})$. (a) for the $H+CH_3F$ reaction; (b) for the $H+CH_2F_2$ reaction; (c) for the $H+CHF_3$ reaction.

proximation as it is sequentially introduced to the exact theory. First, we replaced the full PMP4 single-point energies by the IMOMO ones and the resulting transmission coefficient is denoted as SCT(IMOMO). We obtained nearly identical results. This can be expected since the potential curves from two levels of theory are nearly the same [see Figs. 1(a)–(c)]. Second, in the RC-μi model discussed in Sec. II A 2, we approximate $\mu_{\mathrm{eff}}(s)$ and $V_{\mathrm{int}}(s)$ from those of the principal reaction rather than explicitly calculated; the calculated transmission coefficients agree well with the full results for R1 and R2 and are slightly too small by at most a factor of 4 for R3. Third, in the RC-μV model, instead of explicitly calculating the MEP we approximate $V_a^G(s)$ by scaling that of the principal reaction. We found the calculated transmission coefficients are too small by an order of magnitude. Whether this underestimation is a general observation would require further study on different types of reactions. However, the results indicate that the transmission coefficient is much more sensitive to the $V_a^G(s)$ curve than to the $\mu_{\mathrm{eff}}(s)$ function. For comparison purposes, it is also worthwhile to show the results for the widely used Wigner and Eckart models in conjunction with the TST method. The Wigner model is well-known to greatly underestimate the tunneling contribution. The Eckart model, also known as the zero-order zero curvature tunneling (ZCT-0) method,[30] performs much better than the Wigner with the same computational cost. Theoretically, since it is an approximation of the ZCT method it should be compared to the full ZCT results. In this case, we found it generally overestimates the tunneling contribution due to the fact that the width of the Eckart function is often too small. This leads to a larger transmission probability. However, this error compensates somewhat for the corner cutting effects not included in the model. Consequently, the apparent error of the Eckart model is smaller when compared to the full SCT results. In fact, its performance is slightly better than that of the RC-μV model.

To gain some quantitative sense of the accuracy of different models, we calculated the average ratios of rate constants calculated from different approximate methods to those from the full CVT/SCT results for all three reactions, including both forward and reverse directions. These results are listed in Table II. The IMOMO method is shown to be quite accurate with an average error in the calculated rate constants of at most 7%. Among different tunneling models to be used within the TST framework, the TST/Wigner method greatly underestimates the rate constants particularly at low temperatures as expected. TST/Eckart gives a small apparent error of at most a factor of 5 too small in the rate constant. However, its real error is much bigger, i.e., a factor of 30 too large. In fact, due to cancellation of errors, this

TABLE II. Average ratios of rate constants calculated from different approximate methods to those from full CVT/SCT calculations ($k^{\mathrm{Method}}/k^{\mathrm{CVT/SCT(Full)}}$) for all three reactions (both directions).

T(K)	CVT/SCT (IMOMO)	TST/ Wigner	TST/ Eckart	TST/ RC-μV[a]	TST/ RC-μi[a]
200	1.07	0.0006	0.27(28.4)[b]	0.05	0.81
250	1.06	0.008	0.18(6.9)	0.11	0.72
300	1.05	0.03	0.19(3.5)	0.18	0.69
350	1.04	0.08	0.25(2.5)	0.25	0.68
400	1.03	0.15	0.31(1.8)	0.32	0.69
450	1.02	0.23	0.36(1.9)	0.39	0.71
500	1.02	0.31	0.42(1.7)	0.44	0.72
600	1.0	0.44	0.51(1.6)	0.52	0.75
800	1.0	0.65	0.64(1.5)	0.64	0.81
1000	0.99	0.79	0.71(1.4)	0.71	0.85

[a]Single-point IMOMO energies along the MEP were used.
[b]The values in the parentheses are $k^{\mathrm{TST/Eckart}}/k^{\mathrm{CVT/ZCT(Full)}}$.

TABLE III. A comparison of total computer CPU hours required to study each reaction on an SGI workstation with a single RS 10 000 processor for different models.

Reaction	CVT/SCT (Full)	CVT/SCT (IMOMO)	IST/RC-μi[a]
$H+HCH_2F$	17.3	9.7	3.3
$H+HCHF_2$	34.0	12.8	4.0
$H+HCHF_3$	70.1	15.9	4.1

[a]Single-point IMOMO energies along the MEP were used.

model performs slightly better than the TST/RC-μV model, which gives error of an order of magnitude in the rate constant. Finally, among different models, the TST/RC-μi model gives the smallest error, which is less than 40%. A more important result is that the error of this model show very little temperature dependence, whereas such a dependence is more profound in other models.

Finally, the models introduced here are mainly for computational efficiency. This is clearly demonstrated by the minimal total CPU hours on an SGI RS10 000 workstation required to study each reaction as listed in Table III. The computational cost for the commonly used full CVT/SCT method grows significantly along with the system size, i.e., with the increase in the number of electrons. Using the IMOMO approach instead of performing high-level single-point energy calculations for the whole system drastically reduces the cost. However, such cost is significantly further reduced when we combine the IMOMO approach with the reaction class models. The TST/RC-μi model is shown to be the most cost-effective model, i.e., the lowest price per performance ratio. The total CPU hours are orders of magnitude less than that of full level calculations. More importantly, they show little dependence on the system size or the number of electrons. This fact becomes even more significant as the system size increases. It is important to point out that in this study we have only explored the use of a two-layer IMOMO method. It is possible to extend our methodology to use a multilayer ONIOM approach such as the ONIOM3 method.[32] This certainly will further improve the efficiency of the TST/RC-μi model.

IV. CONCLUSION

In this study, we have introduced a new computationally efficient methodology for calculating rate constants of reactions involving large molecules or a larger number of elementary reactions in the same class. This methodology combines the IMOMO approach with the reaction class models for tunneling. Using the $H+CH_3F$, $H+CH_2F_2$, and $H+CHF_3$ reactions as test cases, we have shown that the new methodology can significantly reduce computational cost by several orders of magnitude while maintaining an acceptable level of accuracy in predicting thermal rate constants. It is possible to further improve the efficiency of the proposed methodology by exploring the use of a multilayer ONIOM approach. With the use of the two-layer IMOMO approach, the TST/RC-μi model, which requires only the geometries and Hessians at the stationary points and the potential energy along the MEP, is shown to be the most cost-effective method for predicting thermal rate constants of large systems. It gives an error of less than 40% across a wide temperature range while the computational cost shows little dependence on the system size or the number of electrons. The practical implication of this method in studying kinetics of large systems or in combustion modeling is in fact enormous. Note that while so far we have only explored the use of the ONIOM method for improving energy, it is also possible to use such a method[48] to provide gradient and Hessian information for rate calculations. This will further improve the efficiency of the approach proposed here. Such a study will be presented in a forthcoming paper.

ACKNOWLEDGMENTS

This work is supported by the University of Utah Center for the Simulation of Accidental Fires & Explosions, funded by the Department of Energy, Lawrence Livermore National Laboratory, under Subcontract No. B341493. We also thank the Utah Center for High Performance Computing for computer time support.

[1] K. K. Baldridge, M. S. Gordon, D. G. Truhlar, and R. Steckler, J. Phys. Chem. **93**, 5107 (1989).
[2] B. C. Garrett, M. L. Koszykowski, C. F. Melius, and M. Page, J. Phys. Chem. **94**, 7096 (1990).
[3] B. C. Garrett and C. F. Melius, in *Theoretical and Computational Models for Organic Chemistry*, edited by S. J. Formosinho, I. G. Csizmadia, and L. G. Arnaut (Kluwer, Dordrecht, 1991), pp. 25–54.
[4] A. Gonzalez-Lafont, T. N. Truong, and D. G. Truhlar, J. Chem. Phys. **95**, 8875 (1991).
[5] W.-P. Hu, Y.-P. Liu, and D. G. Truhlar, J. Chem. Soc., Faraday Trans. **90**, 1715 (1994).
[6] Y.-P. Liu, G. C. Lynch, T. N. Truong, D.-h. Lu, and D. G. Truhlar, J. Am. Chem. Soc. **115**, 2408 (1993).
[7] Y.-P. Liu, D.-h. Lu, A. Gonzalez-Lafont, D. G. Truhlar, and B. C. Garrett, J. Am. Chem. Soc. **115**, 7806 (1993).
[8] K. A. Nguyen, I. Rossi, and D. G. Truhlar, J. Chem. Phys. **103**, 5522 (1995).
[9] D. G. Truhlar, in *The Reaction Path in Chemistry: Current Approaches and Perspectives*, edited by D. Heidrich (Kluwer Academic, Dordrecht, 1995), pp. 229.
[10] T. N. Truong, J. Chem. Phys. **100**, 8014 (1994).
[11] T. N. Truong and W. T. Duncan, J. Chem. Phys. **101**, 7408 (1994).
[12] T. N. Truong and T. J. Evans, J. Phys. Chem. **98**, 9558 (1994).
[13] T. N. Truong, J. Chem. Phys. **102**, 5335 (1995).
[14] R. Bell and T. N. Truong, J. Chem. Phys. **101**, 10442 (1994).
[15] W. T. Duncan and T. N. Truong, J. Chem. Phys. **103**, 9642 (1995).
[16] T. N. Truong, W. T. Duncan, and R. L. Bell, in *Chemical Applications of Density Functional Theory*, Vol. 629, edited by B. B. Laird, R. B. Ross, and T. Ziegler (American Chemical Society, Washington DC, 1996), pp. 85.
[17] Y. Y. Chuang and D. G. Truhlar, J. Phys. Chem. A **101**, 3808 (1997).
[18] J. C. Corchado, J. Espinosagarcia, W. P. Hu, I. Rossi, and D. G. Truhlar, J. Phys. Chem. **99**, 687 (1995).
[19] J. C. Corchado, E. L. Coitino, Y. Y. Chuang, P. L. Fast, and D. G. Truhlar, J. Phys. Chem. A **102**, 2424 (1998).
[20] J. C. Corchado, E. L. Coitino, Y.-Y. Chuang, P. L. Fast, and D. G. Truhlar, J. Phys. Chem. A **102**, 2424 (1998).
[21] B. C. Garrett and D. G. Truhlar, J. Chem. Phys. **70**, 1593 (1979).
[22] D. G. Truhlar and B. C. Garrett, Acc. Chem. Res. **13**, 440 (1980).
[23] D. G. Truhlar, A. D. Isaacson, R. T. Skodje, and B. C. Garrett, J. Phys. Chem. **86**, 2252 (1982).
[24] D. G. Truhlar and B. C. Garrett, Annu. Rev. Phys. Chem. **35**, 159 (1984).
[25] D. G. Truhlar, A. D. Isaacson, and B. C. Garrett, in *Theory of Chemical Reaction Dynamics*, Vol. 4, edited by M. Baer (CRC Press, Boca Raton, FL, 1985), pp. 65–137.

[26] D. G. Truhlar and B. C. Garrett, J. Chim. Phys. Phys.-Chim. Biol. **84**, 365 (1987).
[27] S. C. Tucker and D. G. Truhlar, in *New Theoretical Concepts for Understanding Organic Reactions*, edited by J. Bertran and I. G. Csizmadia (Kluwer, Dordrecht, Netherlands, 1989), pp. 291–346.
[28] D.-h. Lu, T. N. Truong, V. S. Melissas, G. C. Lynch, Y. P. Liu, B. C. Garrett, R. Steckler, A. D. Isaacson, S. N. Rai, G. C. Hancock, J. G. Lauderdale, T. Joseph, and D. G. Truhlar, Comput. Phys. Commun. **71**, 235 (1992).
[29] A. Gonzalezlafont, T. N. Truong, and D. G. Truhlar, J. Phys. Chem. **95**, 4618 (1991).
[30] A. Gonzalezlafont, T. N. Truong, and D. G. Truhlar, J. Chem. Phys. **95**, 8875 (1991).
[31] W. T. Duncan, R. L. Bell, and T. N. Truong, J. Comput. Chem. **19**, 1039 (1998).
[32] M. Svensson, S. Humbel, R. D. J. Froese, T. Matsubara, S. Sieber, and K. Morokuma, J. Phys. Chem. **100**, 19357 (1996).
[33] F. Maseras and K. Morokuma, J. Comput. Chem. **16**, 1170 (1995).
[34] S. Humbel, S. Sieber, and K. Morokuma, J. Chem. Phys. **105**, 1959 (1996).
[35] R. D. J. Froese, S. Humbel, M. Svensson, and K. Morokuma, J. Phys. Chem. A **101**, 227 (1997).
[36] M. Svensson, S. Humbel, and K. Morokuma, J. Chem. Phys. **105**, 3654 (1996).
[37] R. D. J. Froese and K. Morokuma, Chem. Phys. Lett. **263**, 393 (1996).
[38] T. N. Truong and T.-T. T. Truong, Chem. Phys. Lett. (in press).
[39] T. N. Truong, W. T. Duncan, and M. Tirtowidjojo, Phys. Chem. Chem. Phys. **1**, 1061 (1999).
[40] T. N. Truong and D. G. Truhlar, J. Chem. Phys. **93**, 1761 (1990).
[41] D. K. Malick, G. A. Petersson, and J. J. A. Montgomery, J. Chem. Phys. **108**, 5704 (1998).
[42] D. K. Maity, W. T. Duncan, and T. N. Truong, J. Phys. Chem. A **103**, 2152 (1999).
[43] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
[44] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, B. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, GAUSSIAN 98, A.1 ed. (Gaussian, Inc., Pittsburgh, PA, 1998).
[45] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[46] D. E. Woon and T. H. Dunning, Jr., J. Phys. Chem. **98**, 1358 (1993).
[47] C. Gonzalez and H. B. Schlegel, J. Phys. Chem. **94**, 5523 (1990).
[48] S. Dapprich, I. Komáromi, K. S. Byun, K. Morokuma, and M. J. Frisch, J. Mol. Struct.: THEOCHEM **461**, 1 (1999).